Ns6-241-62

NASA CR-59027

Work Function Changes Produced by Chemisorption on Surfaces with Different Types of Adsorption Sites*†

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A simple model describing the changes in work function produced by chemisorption on a surface possessing two types of adsorption sites is presented. Equations for the change in work function as a function of the amount of gas adsorbed are given, and curves for the cases of CO and N_2 adsorbed on the (113) plane of tungsten are compared with recent experimental results.

I. INTRODUCTION

THE changes in work function of metals and semiconductors produced by the adsorption of gases have been investigated for many years and the results have been used in the interpretation of the electronic changes produced at the surface by adsorption. A comprehensive review, including summaries of the concepts, techniques and results of these studies has been presented by Culver and Tompkins.[1]

The change in work function is usually described[1] in terms of the formation of an electrical double layer as a result of the presence of the adsorbate molecules which may possess permanent or induced dipole moments and whose interaction with the adsorbent may result in electron transfer between the admolecules and the solid. If it is assumed that the adsorbed layer at various coverages can be approximated by a double layer of uniform density, the change in work function $\Delta\phi$ can be related[1] to the fractional coverage θ by

$$\Delta\phi = \pm 4\pi N_s M\theta, \qquad (1)$$

where N_s is the number of adsorption sites per cm^2, M is the dipole moment associated with each admolecule, and θ is the fraction of the number of sites N_s occupied. In principle, Eq. (1) can be used to determine M when a plot of $\Delta\phi$ vs θ is found to be linear. A linear change in photoelectric work functions vs θ for values of $\theta < 0.6$ was reported by Baker and Rideal[2] for H_2, CO, and C_2H_4 adsorbed on evaporated metal films of Ta, Fe, Ni, and Co. Culver, Pritchard, and Tompkins,[3] using a diode technique, found that plots of $\Delta\phi$ vs θ for H_2 and CO on evaporated metal films were smooth curves with a decreasing slope rising to a maximum value before the surface was covered. Although properly prepared evaporated films are probably clean, they are

certainly porous, exposing a variety of sites of varying types of interaction with the adsorbate, thereby making agreement with Eq. (1) fortuitous and interpretation questionable.

To make comparison with Eq. (1) significant, it is necessary to consider adsorption and the accompanying $\Delta\phi$ on an array of identical sites, i.e., the face of a single crystal. Such studies have been conducted by Eisinger[4-7] for Co, N_2, H_2, and O_2 adsorbed on a single crystal tungsten ribbon whose surface was normal to the (113) direction. The amount of gas adsorbed was determined by the flash filament technique and the work function was observed photoelectrically. A plot of $\Delta\phi$ vs θ was relatively simple in the case of CO,[4] which showed an initial linear increase in $\Delta\phi$ with θ, rounding to a maximum when the number of adsorbed molecules equaled the number of surface W atoms (2.7×10^{14} cm^{-2}) and then decreasing as adsorption continued. Simple behavior was also reported[5] for N_2, for which $\Delta\phi$ was linear with coverage until the number of adsorbed nitrogen atoms was double the number of surface W atoms, and then there was a sharp increase in slope, $\Delta\phi$ continuing to increase linearly with coverage.

The simple behavior in the cases of CO and N_2 adsorbed on the well-defined surface of tungsten reported by Eisinger clearly suggests that suitable modifications of the ideas involved in Eq. (1) might well make possible detailed interpretations of the adsorption processes in these and similar cases, yielding perhaps values of M which could be associated with single admolecules or adatoms. Eisinger[7] has pointed out that the W atoms in the (113) surface plane are not the only exposed atoms on the surface, but that other W atoms with varying numbers of nearest neighbors are also available. On the basis of a model of an ideal (113) plane he[7] suggested that this plane presents three types of adsorption site for possible interaction with adsorbate molecules. Adsorption was pictured as taking place on these sites consecutively and the scheme was observed to be roughly in accord with the changes in the sticking coefficient with coverage. The existence of

[1] R. V. Culver and F. C. Tompkins, Advances in Catalysis 11, 67 (1959).

[2] M. McD. Baker and E. K. Rideal, Nature 174, 1185 (1954).

[3] R. V. Culver, J. Pritchard, and F. C. Tompkins, *Surface Activity*, edited by J. H. Schulman (Academic Press Inc., New York, 1958), Vol. 2, p. 243.

[4] J. Eisinger, J. Chem. Phys. 27, 1206 (1957).

[5] J. Eisinger, J. Chem. Phys. 28, 165 (1958).

[6] J. Eisinger, J. Chem. Phys. 29, 1154 (1958).

[7] J. Eisinger, J. Chem. Phys. 30, 412 (1959).

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several types of sites may be related to the different states of binding of molecules on tungsten surfaces observed in flash filament studies.[8]

The purpose of this paper is to describe a simple model for the change in work function with coverage for adsorption on a surface possessing equal numbers N_s of different adsorbing sites such as the (113) face of tungsten. It is assumed that adsorption on each type of site results in the formation of a dipole moment M characteristic of that site and that the total change $\Delta\phi$ is then the sum of terms $4\pi N_s M\theta$ for each type of site. While the (113) plane of tungsten apparently possesses three types of site, the model is developed for a surface with two types of sites. The model requires a determination of the relative number of adsorbed molecules on the two types sites, and it will be assumed that adsorption on each type of site simultaneously follows a Langmuir isotherm.[9] Some typical curves for varying possible values of dipole moments on the different sites will be presented and it will be shown that curves giving good agreement with Eisinger's[4,5] data for CO and N_2 on tungsten can be obtained. There is the question of the applicability of Eisinger's flash filament data, which were obtained under nonequilibrium and irreversible circumstances, to a model based on the assumption of a Langmuir isotherm. Some justification for this procedure in this particular case is presented.

II. MODEL

As pointed out above, it is assumed that the adsorbing surface possesses two types of adsorbing sites, denoted A and B. There are N_s sites of each type, and of the possible $3N_s$ sites on the surface, only $2N_s$ will be involved. If there are N_A molecules adsorbed on site type A and N_B molecules adsorbed on site type B, the fractional coverage θ will be defined as $(N_A+N_B)/N_s$ (it is to be noted that θ as here defined is not the number of admolecules divided by the total number of available sites), or letting $\theta_A = N_A/N_s$ and $\theta_B = N_B/N_s$, as

$$\theta = \theta_A + \theta_B. \qquad (2)$$

If it is assumed that adsorption of a molecule on site type A produces a dipole moment M_A and adsorption on site type B a dipole moment M_B, $\Delta\phi$ is expressed by the equation

$$\Delta\phi = 4\pi N_s(\pm M_A\theta_A \pm M_B\theta_B), \qquad (3)$$

where the $\pm$ signs indicate that the orientation of either dipole can be such as to increase or decrease the work function.

Since the total amount of gas adsorbed θ is distrib-

[8] For example, G. Ehrlich, J. Appl. Phys. **32**, 4 (1961).

[9] It is, of course, to be recognized that the assumption of a Langmuir-type isotherm does not imply the Langmuir kinetic mechanism. The isotherm will be assumed here because it has a mathematically simple form and is often empirically useful.
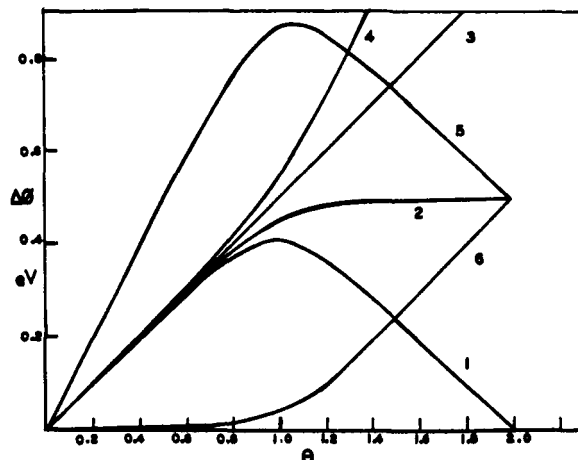
FIG. 1. Curves of $\Delta\phi$ vs θ calculated from Eq. (2), (3), and (4) for $b_A/b_B = 100$ illustrating the consequences of the variety of choices of M_A and M_B (debye units) listed below:

Curve	1	2	3	4	5	6
M_A	+0.357	+0.357	+0.357	+0.357	+0.714	0
M_B	−0.357	0	+0.357	+0.714	−0.357	+0.357

uted over the two types of sites, it is necessary to have a relationship between θ_A and θ_B. As previously explained, we assume that adsorption on each type of site independently follows a Langmuir isotherm. With this assumption, the equilibrium pressure p can be expressed in terms of θ_A and θ_B by

$$p = b_A^{-1}[\theta_A/(1-\theta_A)] = b_B^{-1}[\theta_B/(1-\theta_B)], \qquad (4)$$

giving a relationship between θ_A and θ_B in terms of the ratio of the adsorption coefficients, b_A and b_B.

Equations (2), (3), and (4) can be solved simultaneously to give values of $\Delta\phi$ as a function of θ, for various values of M_A, M_B, and b_A/b_B. In order to illustrate the consequences of different choices of M_A and M_B with regard to sign and magnitude, the curves shown in Fig. 1 have been calculated for the arbitrarily chosen values indicated. In all cases the ratio b_A/b_B was chosen as 100. Increasing the ratio even by an order of magnitude simply sharpens the break in the curves and shifts the region of the break slightly closer to $\theta = 1$. Decreasing the ratio has the reverse effect.

The plot of $\Delta\phi$ vs θ reported by Eisinger[4] for the change in work functions produced by the chemisorption of CO on the (113) plane of tungsten strongly resembles curve 5 of Fig. 1, suggesting that values of M_A and M_B could be found which would produce a curve lying close to the experimental values. Using a value of $b_A/b_B = 100$, a dipole moment $M_A = +0.71$ D (1 D $= 10^{-18}$ esu) and a dipole moment $M_B = -0.28$ D, the solid curve in Fig. 2 was obtained and is to be compared with the experimental points obtained by Eisinger.[4] Adsorption on site type A is pictured as accompanied by electron transfer from the tungsten giving a double layer, increasing the work function. This assumed direction of electron transfer is consistent
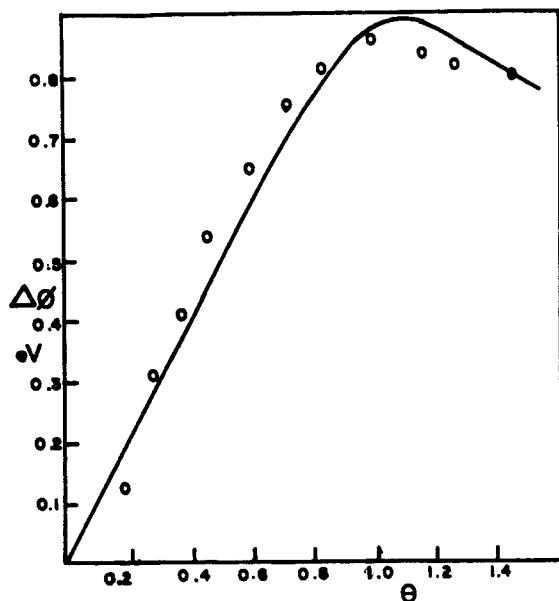
FIG. 2. Plot of change in work function $\Delta\phi$ vs coverage θ calculated from Eq. (2), (3), and (4) with $b_A/b_B = 100$, $M_A = +0.71$ D and $M_B = -0.28$ D compared with experimental points determined by Eisinger[4] for the change in work function of the (113) plane of tungsten due to the adsorption of CO.

cules is frequently accompanied by dissociation of the adsorbate, it is desirable to extend the model to include the possibility of dissociation on one or both sites. Rather than present a general treatment, we will develop the theory for the particular case of molecular adsorption on sites A and atomic adsorption on sites B. It will be shown that this example is strongly suggested in the case of nitrogen adsorbed on tungsten as presented by Eisinger.[5]

In order to allow for dissociation on sites B it will be necessary to redefine θ, the fractional coverage and to introduce the Langmuir isotherm equation for the case of dissociation to obtain equations analogous to (2) and (4). The coverage θ will be defined as the ratio of the total number of adsorbed atoms to the number of sites of each type N_s. If there are N_A sites of type A occupied by molecules and N_B sites of type B occupied by atoms, the total number o fadsorbed atoms is $2N_A + N_B$ and

$$\theta = 2\theta_A + \theta_B, \tag{5}$$

where $\theta_A = N_A/N_s$ and $\theta_B = N_B/N_s$. Using the Langmuir isotherm for the case of dissociation on sites B, Eq. (4) becomes

$$p = b_A^{-1}[\theta_A/1 - \theta_A)] = b_B^{-1}[\theta_B^2/(1 - \theta_B)^2]. \tag{6}$$

with the infrared studies of CO chemisorbed on metals by Eischens and co-workers[10] and with the conductivity investigations of Suhrmann.[11] It is suggested that adsorption on site type B does not result in electron transfer but that it does establish a double layer due to the permanent dipole moment of the CO molecule which is assumed to be oriented so as to produce a decrease in work function. The fact that the required dipole moment is almost three times the permanent dipole moment of CO (about 0.1 D) might be caused by polarization by the field of the adsorbent. An alternative possibility is that absorption on site A might result in a double bond requiring a pair of bonding electrons from the tungsten, while adsorption on type B might result in a single bond giving rise to a dipole with reversed orientation in the manner suggested by Eischens and Pliskin[12] in discussing the interaction of CO with platinum. Infrared investigations of the chemisorption of CO on metals have led Gardner and Petrucci[13] to conclude that adsorbed CO can act as either an electron donor or acceptor, causing either an increase or decrease of the work function.

The model developed above assumes that a single adsorbate molecule adsorbs on a single surface site. Since the chemisorption of diatomic homonuclear mole-

[10] R. P. Eischens, S. A. Francis, and W. A. Pliskin, J. Phys. Chem. 60, 194 (1956).

[11] R. Suhrmann and K. Schulz, Z. physik. Chem. (Frankfort) 1, 69 (1954); J. Colloid Sci. Suppl. 1, 50 (1954).

[12] R. P. Eischens and W. A. Pliskin, Advances in Catalysis 10, 1 (1958).

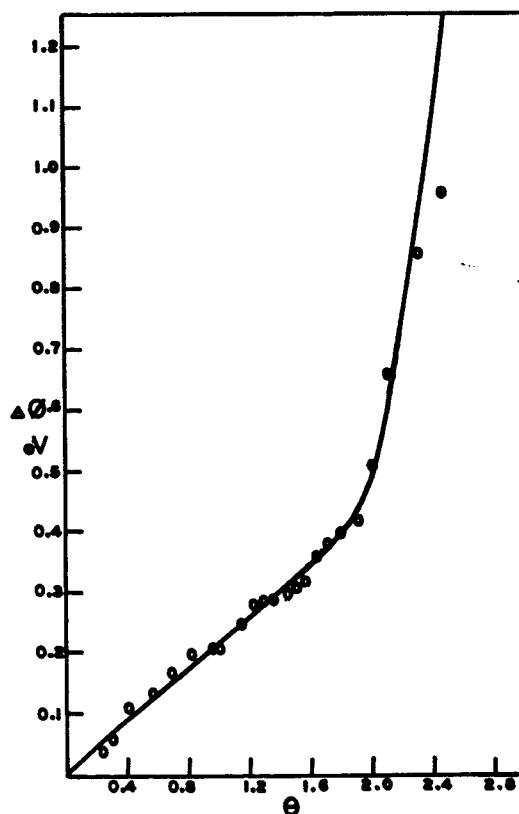[13] R. A. Gardner and R. H. Petrucci, J. Am. Chem. Soc. 82, 5051 (1960).

FIG. 3. Plot of change in work function $\Delta\phi$ vs coverage θ calculated from Eq. (5), (3), and (6) with $b_A/b_B = 10^4$, $M_A = +0.286$ D and $M_B = +1.22$ D compared with experimental points determined by Eisinger[5] for the change in work function of the (113) plane of tungsten due to the adsorption of N_2.

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Letting M_A be the dipole moment due to a molecule adsorbed on site A and M_B be the dipole moment due to an atom on site B, curves of $\Delta\phi$ vs θ can be found from Eqs. (3), (5), and (6). As an illustration of this procedure, the solid curve shown in Fig. 3 was calculated using a ratio of $b_A/b_B = 10^4$ and a dipole moment $M_A = +0.286$ D and $M_B = +1.22$ D. These constants were selected to agree with the results of Eisinger[5] for the adsorption of nitrogen on the (113) plane of tungsten and his experimental points are shown for comparison. In this case, with both M_A and M_B positive, the adsorption process is pictured as being accompanied by electron transfer to the adsorbate in both the molecular and atomic cases. This assumed direction of electron transfer is consistent with the magnetic studies of the adsorption of nitrogen on metals reported by Selwood et al.[14]

III. DISCUSSION

The agreement which can be obtained between the experimental data and the proposed model with the choice of a limited number of constants suggests that the model may reflect some of the essential features of the adsorption mechanism. There is, however, the problem mentioned earlier, of the applicability of an equilibrium model to results based on flash filament data. The flash desorption technique is often[8] used to study the kinetics of desorption by observing the dependence of pressure on time (essentially instantaneous filament temperature) during the flash itself. It is, of course, nonsense to speak of the application of equilibrium concepts while the temperature is changing rapidly. If, however, the filament has been allowed to come to equilibrium at a given temperature and pressure before the flash, and the pressure-vs-time curve is integrated to give the total amount adsorbed before the flash, then, as Kisliuk[15] has shown, steady-state data are obtained. For the case of nitrogen on polycrystalline tungsten, Kisliuk[15] not only determined thermodynamic functions but also showed that the adsorption followed a Langmuir isotherm.

However, in the case of the studies by Eisinger used

[14] P. W. Selwood, S. Adler, and T. R. Phillips, J. Am. Chem. Soc. 77, 1462 (1955).
[15] P. Kisliuk, J. Chem. Phys. 30, 174 (1959).

to illustrate the proposed model, adsorption did not proceed to equilibrium at different pressures and total coverages, but rather adsorption was allowed to proceed for increasing times after a flash until eventually a steady state was reached, which required of the order of hours. There was therefore ample time to obtain the work function at different times and to flash the filament to determine the amount of gas adsorbed at these times, but certainly a steady state had not been established for the individual readings. Equations (4) and (6) represent isotherms and as such imply steady-state conditions, but it is to be noted that in this case the role of p is incidental; only the functional relationships between θ_A and θ_B are relevant. The point here is that not only should Eqs. (4) and (6) be useful under equilibrium conditions, but that it may be plausible to use them to describe instantaneous relationships between θ_A and θ_B before equilibrium is established. For example, in the case of no dissociation [Eq. (4)], assuming constant but different sticking coefficients on sites A and B at low coverages leads to a linear relationship between θ_A and θ_B, as does Eq. (4). At the other extreme, at high coverages as $d\theta/dt \rightarrow 0$, the equations are acceptable as isotherm equations. Hence it seems to the writers that Eqs. (4) and (6) may well represent in simple and convenient form the essential features of the instantaneous relationships between θ_A and θ_B. Indeed, it is questionable whether such satisfactory agreement with experimental data could have been obtained if this were not the case.

The model is in itself subject to the limitations of the other simplified assumptions involved in Eq. (1) and its extension, Eq. (3) as well as in the use of the Langmuir isotherm Eqs. (4) and (6) even under equilibrium conditions. However, the success of the model in determining effective dipole moments giving good agreement with experimental data suggests that elaborate refinements would be unwarranted at the present time.

The extension of the model to three or more sites presents no difficulty, but since almost any functional dependence of $\Delta\phi$ on θ could thus be achieved with a sufficient number of parameters, agreement with experiment would not be as convincing as in the above examples.

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